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The Kinetics and Thermochemistry of
the Thermal Decomposition of the
Initiating Explosive, Tetrazene, near its
Ignition Temperature (between 385 K
and 400 K)

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# The Kinetics and Thermochemistry of the Thermal Decomposition of the Initiating Explosive, Tetrazene, near its Ignition Temperature (between 385 K and 400 K)

*Daniel J. Whelan and Mark R. Fitzgerald*

**Weapons Systems Division**
**Aeronautical and Maritime Research Laboratory**

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## ABSTRACT

The efficient explosive pick-up of the AMRL gasless cap composition based on boron / $Pb_3O_4$ / tetrazene and of many in-service stab- and percussion- sensitive compositions based on primary explosive lead salts mixed with tetrazene arises from the explosive behaviour of tetrazene and its functioning as an energetic sensitizer.

Using the thermoanalytical techniques of differential scanning calorimetry and thermogravimetry, it was established that tetrazene decomposes in a series of steps, close to its ignition temperature, ca. 140°C (413 K); initially, it softens, then it decomposes exothermically in a two-stage process, the first and main stage following an autocatalytic rate law of the form

$$d(\alpha)/dt = k_2 \, \alpha \, (1 - \alpha).$$

where $\alpha$ is the degree of reaction in this first stage, and t, the time.

From an analysis of the kinetics carried out between 387.9 K and 398 K, it has been shown that the kinetics follow an Arrhenius rate dependency, leading to an activation energy (which can be related to the energetics in the bond-breaking processes) of 185.4 kJ $mol^{-1}$ and a pre-exponential factor, related to the entropy of the reaction, ln A ($min^{-1}$), of 56.23.

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DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION

# The Kinetics and Thermochemistry of the Thermal Decomposition of the Initiating Explosive, Tetrazene, near its Ignition Temperature (between 385 K and 400 K)

## Executive Summary

The efficient explosive pick-up of the AMRL gasless cap composition based on boron / $Pb_3O_4$ / tetrazene and of many in-service stab- and percussion- sensitive compositions based on primary explosive lead salts mixed with tetrazene arises from the explosive behaviour of tetrazene and its functioning as an energetic sensitizer.

There has been a continuing interest in the use of these and of related compositions over many years and recent studies into the energetics of the thermal decomposition reactions of related compounds prompted the authors to investigate the kinetic processes involved in the thermal decomposition of tetrazene using the techniques of non-isothermal and isothermal differential scanning calorimetry (DSC) and isothermal thermal gravimetric analysis (TGA).

It was found that the thermal decomposition in the temperature range close to its ignition temperature (ca. 140°C / 413 K) of tetrazene is a complex process, the material appearing to soften prior to decomposition and then decomposing exothermically by a two-stage kinetic process. In the initial, more energetic process, the rate of reaction follows an autocatalytic, bimolecular rate law, which proceeds from interaction between either the reactant and a reactive intermediate (formed from its initial decomposition) or the solid in the presence of melt. This is relatively uncommon amongst organic compounds and may help to explain the effectiveness of tetrazene as a primary booster explosive.

The energy of activation of the thermal decomposition of tetrazene is 185 kJ mol$^{-1}$, a value consistent with that found for other similar primary boosters (for example, tetryl).

Appreciation of these results should will enable modellers to reconstruct more realistic descriptions as to how the energy output of ordnance fitted with the AMRL gasless igniter caps will vary in an ignition train.

# Authors

## D.J. Whelan
Weapons Systems Division

*Dan Whelan joined AMRL in 1968 and worked in various areas of Organic Chemistry Division before transferring to the forerunner of Explosives Ordnance Division in 1980. His current interests are in explosives performance, underwater explosives, thermal analysis, solid state reaction kinetics and practical data correlations. He is on the Editorial Board of the Journal of Energetic Materials.*

## M.R. Fitzgerald
Weapons Systems Division

*Mark Fitzgerald joined MRL in 1978 and has worked in both the explosive and pyrotechnic areas. He is currently working on the thermal analysis of energetic materials.*

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# 1. Introduction

The efficient explosive pick-up of the AMRL gasless cap composition based on boron / $Pb_3O_4$ / tetrazene and of many stab- and percussion- sensitive compositions based on primary explosive lead salts mixed with tetrazene [1-5] arises from the explosive behaviour of tetrazene and its functioning as an energetic sensitizer [1-4].

There has been a continuing interest in the use of these and of related compositions over many years [6] and recent studies into the energetics of the thermal decomposition reactions prompted the authors to investigate the processes involved in tetrazene using the techniques of non-isothermal [7-11] and isothermal [11-13] differential scanning calorimetry (DSC) and isothermal thermal gravimetric analysis (TGA) .

Apparent inconsistencies in earlier work [9-11] prompted the present authors to reassess what had been reported and to redo work as necessary. It can now be reported that the overall thermal decomposition pathway of tetrazene is not simple and that, near its ignition temperature (ca.140°C, 413 K), it proceeds through several stages.

Initially, tetrazene appears to soften rather than to melt (a situation confirmed by thermal hot-stage microscopy as well as by isothermal as well as dynamic differential scanning calorimetry) and then to undergo an exothermic decomposition reaction. This latter process is accompanied by a net heat output of $398 \pm 36$ J g $^{-1}$ as well as a loss of ca. 14 % of the initial mass. It follows a well-developed sigmoidal kinetic rate profile, which is similar to that observed in the thermal decomposition of many organic compounds [14 - 16] including that of another sensitive booster explosive, tetryl [12].

Over the range 385 K to 400 K, the reaction shows an Arrhenius temperature dependency with an activation energy of 185 kJ mol$^{-1}$ and a preexponential factor of $\log_{10} [A, s^{-1}]$ of 24.42 with a linear least squares coefficient of determination of 0.997.

There is a second stage of the observed decomposition reaction from tetrazene in this temperature range. This second stage is considerably slower than the first but, in its early stages, it overlaps the latter part of the initial reaction. It may be associated either with further decomposition of the products of the initial reaction or an independent decomposition pathway for the tetrazene molecule. The total mass loss observed and the net heat output in this second stage depend on the temperature of the reaction.

# 2. Chemical Structure of Tetrazene

The structure of tetrazene has yet to be established unequivocally [17-19]. On the basis of the most reliable chemical evidence [17], either of the structures I(a) or I(b) can be supported:-

I(a)

I(b)
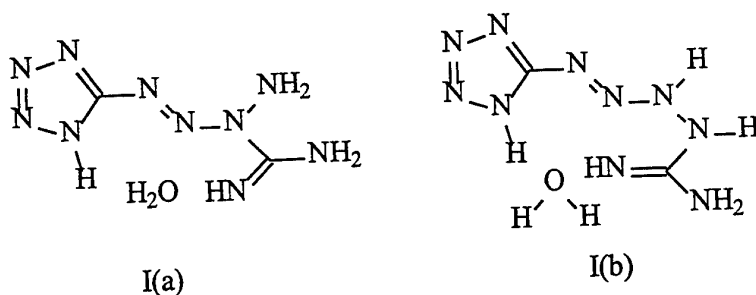
# 3. Materials

Tetrazene was prepared via diazotization and coupling of $N$-aminoguanidine.$HNO_3$ (2 mol) by acidified sodium nitrite (1 mol) in water at 0 - 4°C or by diazotization of 5-aminotetrazole (1 mol) with acidified sodium nitrite (1 mol) and subsequent, *in-situ* coupling with $N$-aminoguanidine.$HNO_3$ [or $H_2SO_4$]$_½$ (1 mol) [17]. Both approaches yield tetrazene which precipitates out. It is a very pale yellow, fine, coherent but powdery product, which is very insoluble in water and most common solvents. It melts with vigorous decomposition around 140°C, the actual temperature depending on the heating rate.

# 4. Differential Scanning Calorimetry

The techniques of isothermal and non-isothermal differential scanning calorimetry (DSC) were principally employed in this study and the results corroborated from isothermal thermal gravimetry (TGA).

DSC measurements were carried out using a power-compensated, Perkin Elmer Model DSC2-C Differential Scanning Calorimeter controlled by a Perkin Elmer Model 3600 Data Station with appropriate software. All samples (approx. 0.7 - 1.1 mg) were accurately weighed on a Mettler ME30 Microanalytical Balance directly into aluminium sample pans and lids placed (not crimped) over the samples. The sample and reference compartments of the calorimeter were continuously purged with

nitrogen throughout the DSC scans, the gas flow rate typically being 15 - 20 ml min$^{-1}$, nominally at atmospheric pressure.

Non-isothermal DSC was carried out at different heating rates, as previously described [8].

Isothermal DSC runs were carried out following the general procedure described in the Perkin Elmer software package, "Isotherm", using a heat ramp of 40 K min$^{-1}$ to bring the sample directly from ambient temperature to the final temperature. This package, however, is limited in its ability to report corrected data from DSC traces of complex reactions or traces from reactions where the thermal output / baseline must be adjusted as a result of significant changes in the heat capacity and the mass of the sample which may occur during an experiment. As a consequence, the raw data stored in "Isotherm" was transferred, using the Perkin Elmer package, "Conversion", to an IBM-compatible computer for processing and subsequent manipulation, using routines which plot corrected heat output (and related functions) vs. time, (Table 1 and Fig.1a and 1b).

Isothermal TGA was carried out on a Polymer Laboratories / Stanton Redcroft Simultaneous (DTA/TGA) Thermal Analyser, Model STA 1500. The output of the thermal analyser was coupled directly to a data logger, so connected as to record the sample mass (uncorrected for buoyancy effects) and the temperatures of both the sample and reference pans. The sample mass was typically 1.0 to 1.8 mg and the system continuously purged with nitrogen. The system was ramped at 10 K min$^{-1}$ (to limit the thermal inertia inherent in the instrument) to a predetermined nominal furnace temperature.

The sample temperatures were calibrated using $KNO_3$ and indium standards [20].

# 5. Results: DSC Traces from Tetrazene

The non-isothermal DSC trace of tetrazene is given in Fig. 2.

The trace obtained from samples heated at 5 K min$^{-1}$ consists of three main features,

a) an apparently inconspicuous but very relevant onset to an endothermic transition from 405 to 407 K (attributed to softening or the onset of melting), and

b) a series of two strong exotherms spanning the temperature range 407 K and 470 K.

The first exotherm consists of two peaks, at 413.5 K and at 416.5 K (variation ± 1.0 K), and is attributed to two, almost concurrent processes, namely, the thermal decomposition of tetrazene itself, and the subsequent decomposition of a primary

decomposition product, the measured heat of reaction for this combined exotherm being $590 \pm 20 \, \text{J g}^{-1}$.

The measured heat of reaction associated with the much broader, second exotherm, which spans the temperature range from ca. 418 K out to 470 K, is $630 \pm 50 \, \text{J g}^{-1}$. The estimated variations are based on measurements from seven different samples of tetrazene.

These non-isothermal DSC traces are similar to those reported elsewhere [3].

The isothermal DSC trace of tetrazene at 390.6 K [117.4 K] (Fig. 1a and 1b and Table 1) is typical of that obtained at other temperatures.

If no reaction were occurring, the slope of the curve, heat evolution per unit time (the ordinate, dQ / dt) vs. time (the abscissa, t), should be zero. As it turns out, the slope in the domain, designated AB, is greater in magnitude than that in the domain YZ. This is consistent with a gradual uptake of heat by the softening tetrazene in the initial period. The slope YZ probably parallels the heat capacity uptake of the residue from the reactions occurring between B and Y.

At B, the onset of thermal decomposition becomes apparent.

In the time domain, BC, it was assumed that the reaction is due solely to the first half of the thermal decomposition of the tetrazene and that the apparent maximum in the heat output process, C, represents approximately the 50 % point in this reaction. By intuitively selecting point D such that the area under the curve bounded by BC'D is twice that bounded by BMC', one can analyse the reaction kinetics in terms of exothermic heat loss vs. time for the domain BC', where C' is an off-set value of C and corresponds to the coordinate for the maximum rate of heat evolution for the first exotherm.

Without forcing the data to conform to this model, consistent data were obtained for all the experiments carried out, the total heat output for the first exotherm (being twice that for the various areas BMC') being $398 \pm 36 \, \text{J g}^{-1}$ (measured as $95.1 \pm 8.5 \, \text{cal g}^{-1}$).

The experimental data for the plot of the heat evolved assuming that this stage of the reaction represents a true Stage 1 of a multi-step process is given in Table 2.

This approach tacitly assumes that the experimental data will fit a relationship which has a maximum heat output per unit time at 50% reaction [21] and almost forces the data to be fitted to a relationship of the form

$$d(\alpha)/dt = k_2 \, \alpha \, (1 - \alpha)$$

or, in integrated form, $\quad k_2 (t - t_{0.5}) = \ln [\alpha / (1 - \alpha)]$

4

where

t is the time,

$t_{0.5}$ is an integration constant, corresponding to the time at which 50 % of the reactant is consumed,

$\alpha$ is the fractional extent of the reaction under examination. It is the fractional decomposition of the reactant, as defined in this study by the heat evolved in the reaction at time, t, relative to that represented by the boundary BC'CD (Fig. 3), and

$k_2$ is a nominal 2nd order rate constant, appropriate to the particular reaction.

The rate constants at the various temperatures studied in this report are presented in Table 3. That they fit an Arrhenius plot so well (Footnote to Table 3) reinforces the justification for the approach employed herein.

A similar conformity as to the rate profile was obtained from isothermal thermogravimetry at 399 K (uncorr.). The mass loss over this first stage was approx. 14 % of the total mass of the starting sample.

From the isothermal DSC data in Table 3, one obtains an Arrhenius activation energy for the reaction of 185.4 kJ mol$^{-1}$, and pre-exponential, ln A (min$^{-1}$) of 56.2336.

From these data, a linear plot of ln ( $k_2$ [min $^{-1}$] ) vs. 1 / T(K) is obtained, with an intercept, ln ( $k_2$ [min $^{-1}$] ) at 1/T = 0 K or ln A (min $^{-1}$), of 56.2336 and a slope of -22.295, with a linear least squares coefficient of determination of 0.9968. This leads to an Arrhenius activation energy for the reaction under investigation of 185.4 kJ mol$^{-1}$, and pre-exponential, ln A (min$^{-1}$) of 56.2336.

To confirm that the reaction being followed in this stage of the thermal decomposition is related to the overall reaction seen under non-isothermal DSC conditions (Fig. 2), duplicate experiments were carried out where the reaction was followed through the first stage of the thermal decomposition at 390.6 K (ie., up to M on Fig. 1) and then quenched by cooling to room temperature.

The heat of reaction evolved in the first stage was in the range reported earlier, viz., 398 ± 36 J g $^{-1}$ of original sample. The partially-spent sample was then reheated at 5 K min$^{-1}$ over the temperature range from ambient to beyond 430 K where the DSC trace (Fig. 4) indicated that:

a) the heat evolved over the temperature range 375.8 K to 416.3 K was 176 ± 8 J g $^{-1}$ (duplicate experiments),

and, somewhat unexpectedly,

b) the temperature of maximum heat output of the exotherm (406.9 K) was less than those in the tetrazene DSC trace (412 K and 416 K), carried out at the same heating rate. This was reminiscent of similar findings by Maksacheff and Spear [9] who suggested intuitively that the thermal ageing of several primary explosives at 89°C (362 K) is an autocatalytic process.

The combined heat evolved from this latter set of reactions is $574 \pm 44$ J g$^{-1}$, a range which overlaps with that corresponding to the thermal decomposition of tetrazene, $590 \pm 20$ J g$^{-1}$, as determined from the experiment illustrated in Fig. 1 and 2.

This ties in with a similar study reported by Patel and Chaudhri [11], who found that the heat output from tetrazene decomposition over a similar temperature range to be $603 \pm 63$ J g$^{-1}$ (uncrimped pans, flowing $N_2$).

# 6. Discussion

As mentioned in the Introduction, tetrazene, on heating near its thermal ignition temperature, initially appears to soften rather than to melt; this is confirmed by thermal hot-stage microscopy as well as by examination of the dynamic DSC traces at slower heating rates. The material glistens but it is only as the decomposition proceeds does one become aware that the material may be softening / melting prior to decomposing rather than decomposing from the solid state. This decomposition is accompanied by the formation of a darkened liquid phase, bubbling and the evolution of gas. This suggests that, while the initial reaction may be occurring from the solid state, the eventual reaction may be proceeding from the liquid state, either directly or from dissolution of the solid into the liquid state.

Among the earliest reports on the behaviour of the thermal decomposition of tetrazene is the study of Yoffe [Ref. 21 , also quoted in Ref. 14]. Yoffe believed that tetrazene did not melt but decomposed with the liberation of gaseous products and that only as the decomposition proceeded did the material soften. The results reported by the present authors are more equivocal as to the role of a melting, liquid phase reaction.

In the early literature on the isothermal decomposition of tetrazene, it was assumed that the heat output (as measured by Patel and Chaudhri, [11]) and evolved gas (as measured by Joyner, [6]) over the complete passage of time were associated with a single reaction sequence and that the kinetics could be described by a single rate law, over the temperature range to 413 K (140° C) [6, 11]. The current study belies that conclusion.

Above 400 K, the present authors found it impossible to monitor the heat output / time profile with the necessary accuracy required for meaningful DSC analysis while above ca. 405 K, the reaction proceeded just far too quickly for the power-

compensated DSC to retain thermal equilibrium once the reaction got underway [13 b, c].

In addition, it would appear as if the thermal output, as measured by Patel and Chaudhri [11] in an earlier DSC study, was monitored with a Perkin Elmer power-compensated DSC-2 instrument, its output being processed through a chart recorder. Such output invariably required adjustment of base lines by a manual procedure; as a result, it is possible that any departures from linearity in response from the recorder and any possible limitations in adjusting baselines could have masked the fact that there were in reality two (or more) decomposition reactions taking place, not one.

That same conclusion was reached by Joyner; in manometric studies over the temperature range from 363 K to 403 K (90°C to 130°C) , he found that for the first stage his $\alpha$ vs. t ($\alpha$) plots were sigmoidal. However, from the record of his presentation [6], one could not discern the rate law describing the kinetics behind that plot. Joyner determined the Arrhenius activation energy behind that reaction, 197 $\pm$ 10 kJ mole$^{-1}$ and an Arrhenius preexponential , ln A (min$^{-1}$) of 73. These figures indicate that decomposition takes place quickly and at a low temperature; however, the magnitude of the pre-exponential term is misleading; it is very dependent on the rate law used to describe the reaction kinetics being followed. The present authors have raised this issue in an earlier publication on the thermal decomposition of dipicryloxadiazole, DPO [13c].

Sheng and Huang carried out their analyses on non-isothermal DSC data obtained from tetrazene in sealed pans [10]. They too were able to synthesise a sigmoidal plot (albeit for the whole of what the present authors have designated Stages 1 and 2) from the relationship, extent of reaction ($\alpha$) vs. reduced time (t ($\alpha$) / t (0.5)), where t($\alpha$) was the time taken to reach a fractional loss of reactant, $\alpha$, at a particular heating rate, starting at the same temperature.

However, from their analysis, they suggested that the thermal decomposition of tetrazene does not really follow a sigmoidal rate law but rather a rate law of the form

$$d(\alpha)/dt = k^{\rightarrow} (1 - \alpha)^{3/2} \qquad \text{[eq. 3]}$$

which gives, on integration,

$$k^{\rightarrow} (t - t_{0.5}) = 2(1 - \alpha)^{-1/2} - 2\sqrt{2} \qquad \text{[eq. 4]}.$$

This can be compared to the rate equations which the present data fits very well, viz.

$$d(\alpha)/dt = k_2 \alpha (1 - \alpha) \qquad \text{[eq. 1]}$$

or, in integrated form,

$$k_2 (t - t_{0.5}) = \ln[\alpha / (1 - \alpha)] \qquad \text{[eq. 2]}.$$

In both these cases, t = $t_{0.5}$ when $\alpha$ = 0.5.

The experimental data from the current study is given in Table 2; how unsatisfactorily these data fits Eq. 4 and how well it fits Eq. 2 can be seen from inspection of Figs. 5 and 6.

A priori, Eq. 3 (from Sheng and Huang [10]) suggests that a maximum reaction rate occurs at t = 0, an observation which is inconsistent with the sigmoidal $\alpha$ vs. t plot which the current authors have found.

To reconcile these two situations, the current authors propose that there must be different kinetic mechanisms operating. Sheng and Huang were studying the thermal decomposition of tetrazene in a confined environment, the present authors were studying the same reaction in an effectively open environment.

Interestingly, Sheng and Huang determined from the data calculated in their study, the activation energy to be 184 kJ mole$^{-1}$, a value almost identical with the one established in this work, 185 kJ mole$^{-1}$ and one not too far removed from what Joyner found, 197 ± 10 kJ mole$^{-1}$ [6]. This strongly suggests that, in the two processes, the same chemical bonds are being broken in the rate determining step from similar transition states; however, the fact that the reactions are following different kinetic schemes (Eq. 3 and Eq. 1) implies that the steps through which the reactions are proceeding are different.

In the study carried out by Sheng and Huang, the diffusion of gaseous products away from the reactants may be the controlling factor in the decomposition process and that, in their sealed pan experiments, the enclosing of these gaseous products slowed down the decomposition. That proposal is reasonable, even though it takes no consideration of the effect of the build up of pressure *per se* on the reaction kinetics; it is quite possible that Sheng and Huang's analysis does have merit for reactions carried out in a confined and sealed environment.

In the present study, the kinetic profile is consistent with the fact that the rate of reaction follows an autocatalytic rate law [14, 23]. That being so, either the reaction can be deemed to be proceeding either from a bimolecular interaction between the reactant and a reactive intermediate (formed from its initial decomposition) or from a solid / melt or related interaction [14].

In a previous study from this laboratory [24], Bird and Power studied the thermal decomposition of tetrazene in a vacuum tube, under closed and static conditions at 90°C (0.1 g) [Experiment 4.2.3 of that Report]. The rate of gas evolution followed a sigmoidal $\alpha$ vs. time kinetic profile but the reaction was much slower than that expected on the basis of the Arrhenius reaction rate constants presented in this report. This reinforces the basic premise of Sheng and Huang's study [10], namely that the gaseous products from the thermal decomposition can inhibit the rate of the overall reaction.

Bird and Power [24] also found that an azide-containing moiety (IR and UV spectra), possibly guanyl azide, Structure 2, appears to be formed as an intermediate in the reaction and that, amongst the end products, one obtains from 1 mol tetrazene, 1.7 mol 5-amino-tetrazole, Structure 3 [25]. Using ^{15}N labelling, it was established that this latter product arose both from the tetrazole ring, which apparently remains intact in the thermal decomposition, and from the side chain of the tetrazene molecule.
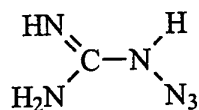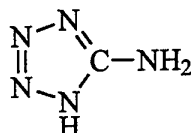


II                                               III

The stoichiometry of the reaction determined by Bird and Power,

   1 mol  tetrazene (I) → 1.7 mol anhydrous 5-amino-tetrazole (III),

requires a mass loss of 24 %.

From isothermal TGA at a nominal 399 K (uncorr.), Fig. 7, after approx. 80 minutes, the mass loss from tetrazene was found to be 26 %, from a sample of original mass 1.24 mg. Thereafter, mass was lost, more or less following relatively slow, zero-order kinetics out to beyond 135 minutes, where the present study ceased. It is plausible that one of the products from the thermal decomposition reaction of tetrazene was, indeed, 5-aminotetrazole, III [25], even though the remaining material in the TGA and the DSC pans from this study appeared to be a sticky residue.

These results are also consistent with what Joyner reported [6]. He found that the principal products of the reaction were nitrogen, water, 5-aminotetrazole and an unidentified solid residue, possibly containing the azido function. It would be surprising if the nitrogen released in the thermal decomposition would inhibit further reaction or alter the path of the reaction to the extent suggested by Sheng and Huang's approach but that matter was not pursued.

# 7. Conclusion

There is probably no conflict between the work described in the more comprehensive studies described here and elsewhere [6, 10, 11, 24] on the thermal decomposition of tetrazene below its ignition temperature, save and except that it has been established that the reactions taking place are complex and the kinetic pathways depend on the degree of confinement and the environment of the material.

In the present study where the behaviour of tetrazene in an unconfined state and in a stream of nitrogen was monitored by isothermal differential scanning calorimetry, it is

probable that the first stage of the thermal decomposition of tetrazene is occurring either from the melt or at the solid / melt interface [14] and that the kinetics can be explained by an autocatalytic reaction of the form

$$d(\alpha)/dt = k_2 \alpha (1 - \alpha) \qquad [\text{eq. 1}].$$

From an analysis of the kinetics carried out between 387.9 K and 398 K, it has been shown that the kinetics follow an Arrhenius rate dependency, leading to an activation energy (which can be related to the energetics in the bond-breaking processes) of 185.4 kJ mol$^{-1}$ and a pre-exponential factor, related to the entropy of the reaction, ln A (min$^{-1}$), of 56.23.

One can tie up this work with that described some 18 years ago by Bird and Power [24], who found that the principal product from the thermal decomposition of tetrazene at 363 K was probably 5-aminotetrazole and that the reaction proceeded, at least in part, through an intermediate, guanyl azide. As in the present study, Bird and Power's results followed a sigmoidal $\alpha$ vs. t rate profile.

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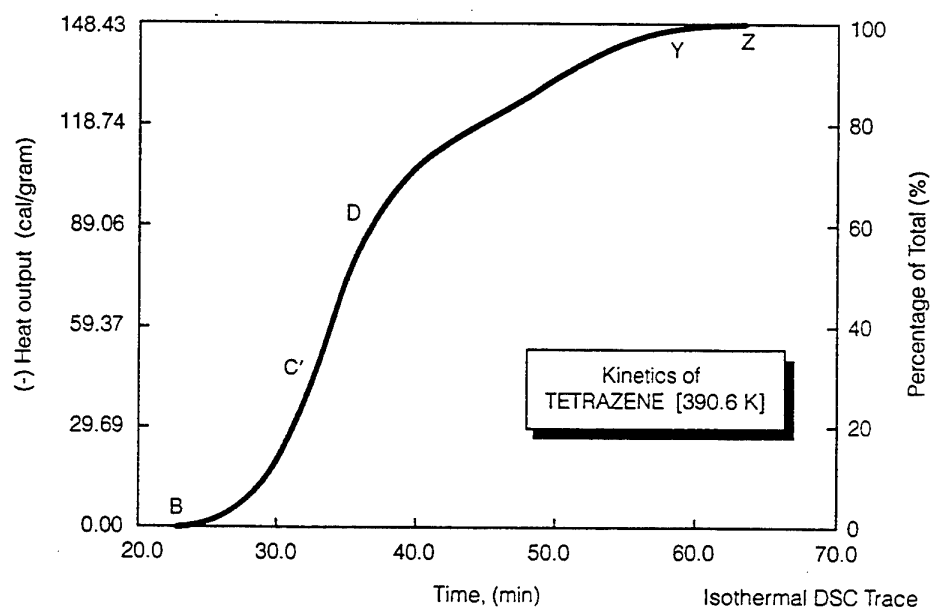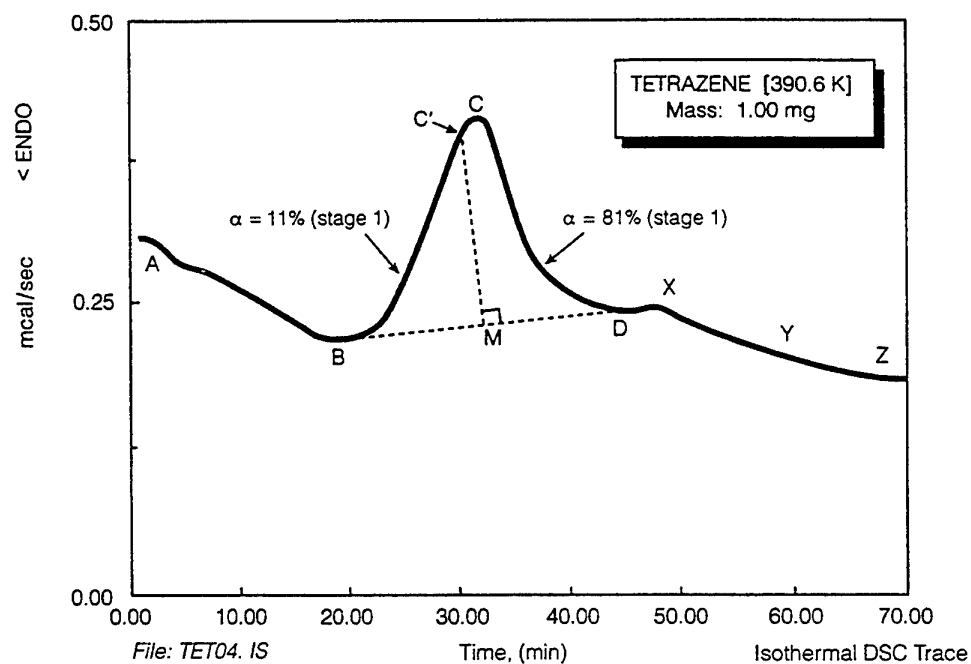
*Figure 1.* *The thermal output of the isothermal power-compensated DSC trace of tetrazene at 390.6 K [117.6° C] in a covered Al sample pan under a stream of nitrogen for the first two stages of the reaction.*

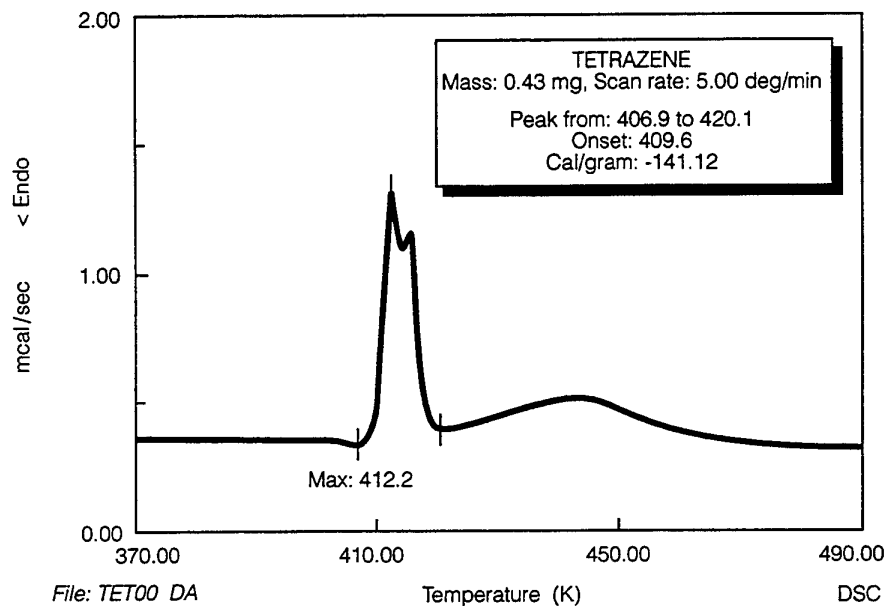*Figure 2.* The non-isothermal power-compensated DSC trace of tetrazene, heated at 5 K min$^{-1}$ in a covered (but uncrimped) Al sample pan under a stream of nitrogen.
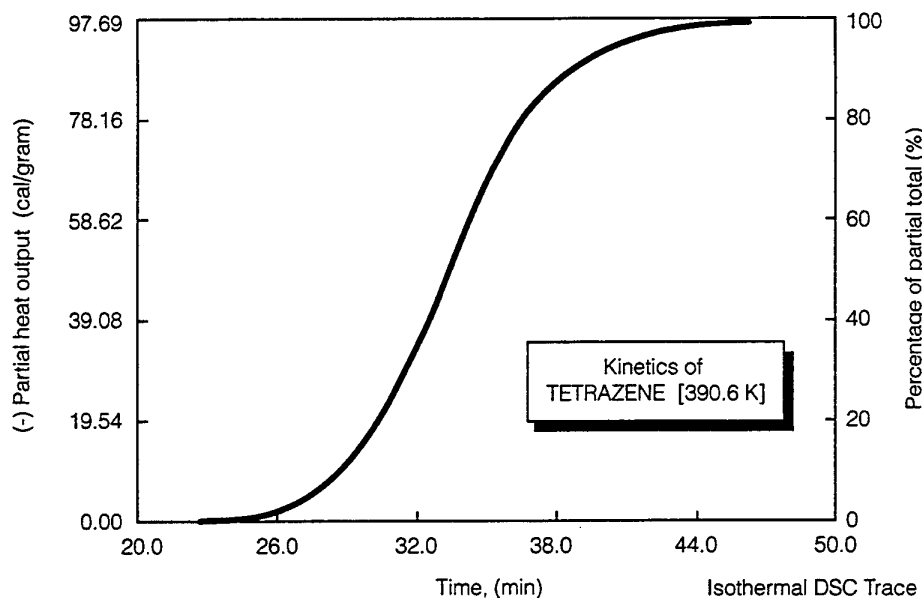


*Figure 3.* The isothermal power-compensated DSC trace of Stage 1 in the thermal decomposition of tetrazene at 390.6 K in a covered Al sample pan under a stream of commercial oxygen-free nitrogen gas.
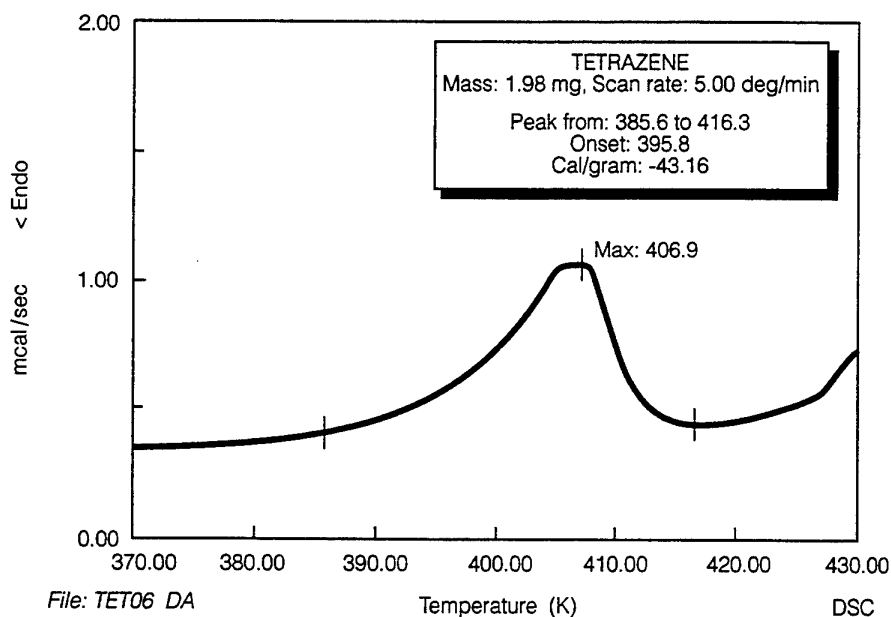
*Figure 4. The non-isothermal DSC trace of tetrazene previously heated at 390.6 K through the 1st stage of thermal decomposition, cooled to room temperature and then reheated at 5 K min⁻¹ in a covered Al sample pan under a stream of nitrogen.*
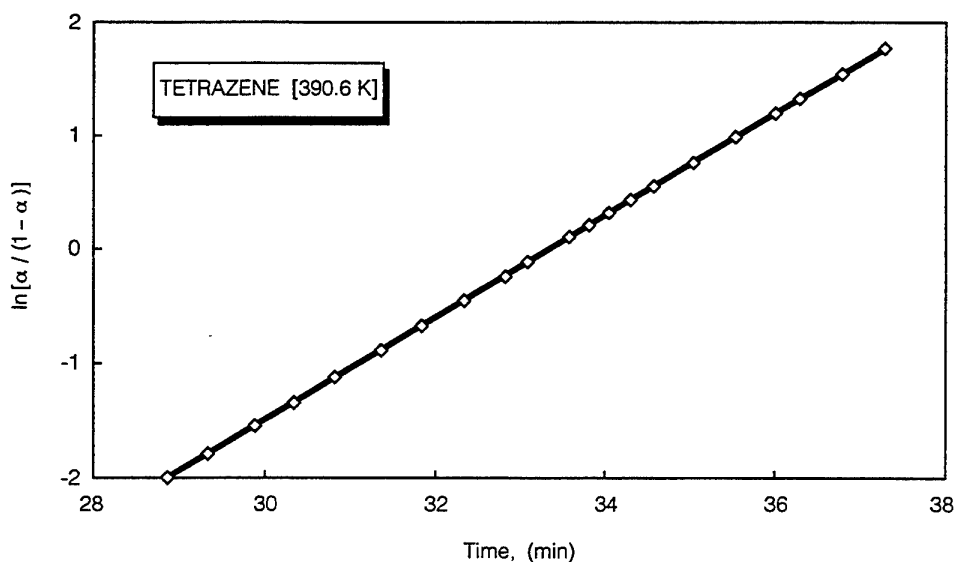


*Figure 5. The fit of the experimental data from Table 2 for the thermal decomposition of tetrazene at 390.6 K in relation to Equation 2, the autocatalytic rate law [14] for 84.4 % > α > 11.5 %. The LLSQ coefficient of determination for the straight line of best fit is 0.9995.*
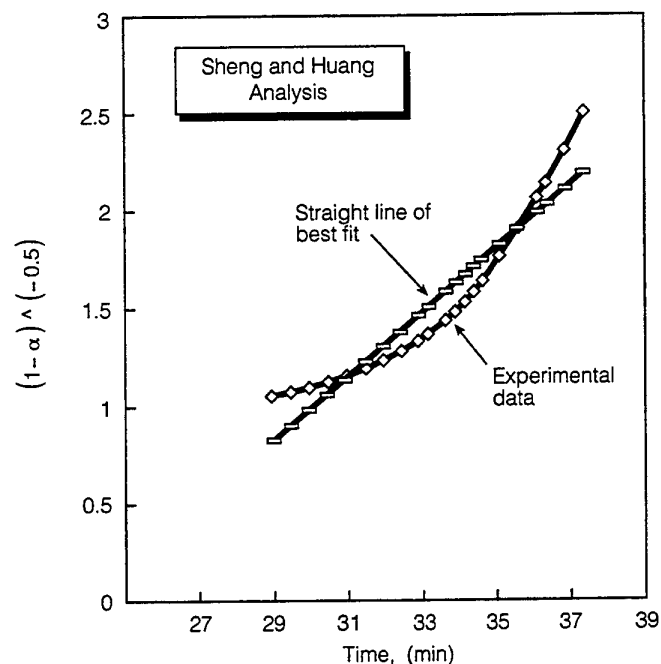
*Figure 6.* The fit of the experimental data from Table 2 for the thermal decomposition of tetrazene at 390.6 K in relation to Equation 4, following Sheng and Huang [10] for 84.4 % > α > 11.5 %. The LLSQ coefficient of determination for the straight line of best fit is 0.8915 but the straight line of best fit is not an acceptable trend line for the reaction under study.



*Figure 7.* The thermogravimetric trace of the isothermal decomposition of tetrazene at 399 K (uncorr.) in a Pt sample pan under a slow stream of commercial oxygen-free nitrogen gas.

Table 1.    *The heat evolved in the thermal decomposition of tetrazene in uncrimped aluminium pans, in a stream of nitrogen at 390.6 K over the first sixty minutes of the reaction.*

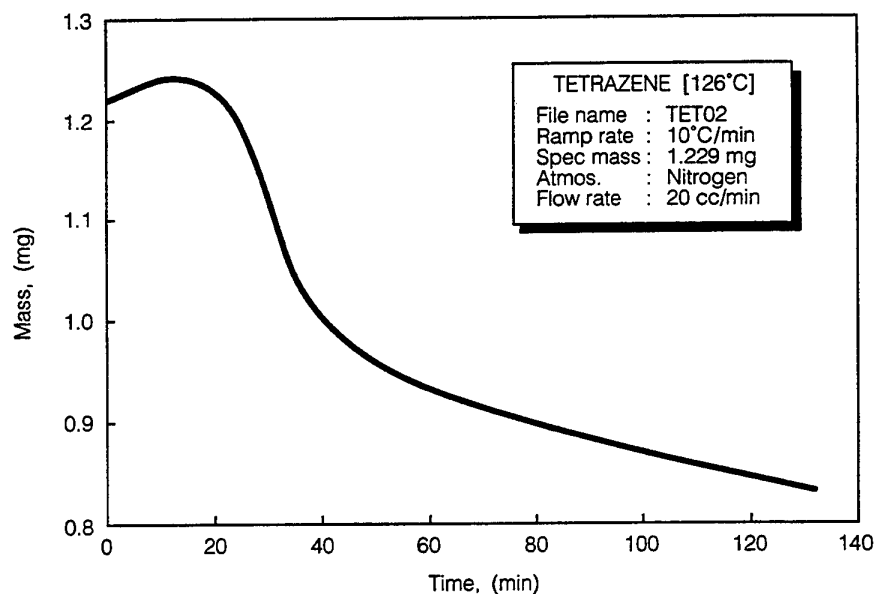| Time (min.) | Heat evolved (cal/g) | Time (min.) | Heat evolved (cal/g) | Time (min.) | Heat evolved (cal/g) |
|---|---|---|---|---|---|
| 21.95 | 0.03 | 29.85 | 20.53 | 37.74 | 96.87 |
| 22.20 | 0.06 | 30.09 | 22.41 | 37.99 | 98.20 |
| 22.45 | 0.10 | 30.34 | 24.41 | 38.23 | 99.46 |
| 22.69 | 0.16 | 30.59 | 26.46 | 38.48 | 100.68 |
| 22.94 | 0.24 | 30.83 | 28.64 | 38.73 | 101.82 |
| 23.19 | 0.34 | 31.08 | 30.94 | 38.97 | 102.94 |
| 23.43 | 0.45 | 31.33 | 33.35 | 39.22 | 103.98 |
| 23.68 | 0.57 | 31.57 | 35.85 | 39.47 | 105.05 |
| 23.93 | 0.72 | 31.82 | 38.48 | 39.71 | 106.01 |
| 24.17 | 0.90 | 32.07 | 41.17 | 39.96 | 106.94 |
| 24.42 | 1.10 | 32.21 | 43.92 | 40.21 | 107.85 |
| 24.67 | 1.33 | 32.56 | 46.78 | 40.45 | 108.69 |
| 24.91 | 1.60 | 34.04 | 49.64 | 40.70 | 109.55 |
| 25.16 | 1.95 | 33.05 | 52.56 | 40.95 | 110.36 |
| 25.41 | 2.30 | 33.30 | 55.53 | 41.19 | 111.17 |
| 25.65 | 2.68 | 33.55 | 58.47 | 41.44 | 111.95 |
| 25.90 | 3.13 | 33.79 | 61.43 | 41.69 | 112.94 |
| 26.15 | 3.64 | 34.04 | 64.37 | 41.93 | 113.48 |
| 26.39 | 4.21 | 34.29 | 67.26 | 42.18 | 114.21 |
| 26.64 | 4.82 | 34.53 | 70.10 | 42.43 | 114.91 |
| 26.89 | 5.52 | 34.78 | 72.83 | 42.67 | 115.59 |
| 27.13 | 6.30 | 35.03 | 75.49 | 42.92 | 116.26 |
| 27.38 | 7.17 | 35.27 | 78.06 | 43.17 | 116.90 |
| 27.63 | 8.10 | 35.52 | 80.47 | 43.41 | 117.52 |
| 27.87 | 9.12 | 35.77 | 82.75 | 43.66 | 118.16 |
| 28.12 | 10.20 | 36.01 | 84.90 | 43.91 | 118.77 |
| 28.37 | 11.40 | 36.26 | 86.95 | 44.15 | 119.35 |
| 28.61 | 12.68 | 36.51 | 88.86 | 44.40 | 119.90 |
| 28.86 | 14.05 | 36.75 | 90.69 | 44.45 | 120.43 |
| 29.11 | 15.51 | 37.00 | 92.40 | 44.89 | 120.97 |
| 29.35 | 17.08 | 37.25 | 93.98 | 45.14 | 121.51 |
| 29.60 | 18.75 | 37.49 | 95.46 | continued, next page | |

*Table 1 (continued).* The heat evolved in the thermal decomposition of tetrazene in uncrimped aluminium pans, in a stream of nitrogen at 390.6 K over the first sixty minutes of the reaction.

| Time (min.) | Heat evolved (cal/g) | Time (min.) | Heat evolved (cal/g) | Time (min.) | Heat evolved (cal/g) |
|---|---|---|---|---|---|
| 45.39 | 122.04 | 50.57 | 133.19 | 55.75 | 141.13 |
| 45.63 | 122.58 | 50.81 | 133.72 | 55.99 | 141.35 |
| 45.88 | 123.11 | 51.06 | 134.24 | 56.24 | 141.53 |
| 46.13 | 123.61 | 51.31 | 134.75 | 56.49 | 141.70 |
| 46.37 | 124.11 | 51.55 | 135.20 | 56.73 | 141.88 |
| 46.62 | 124.60 | 51.80 | 135.64 | 56.98 | 142.07 |
| 46.87 | 125.08 | 52.05 | 136.11 | 57.23 | 142.22 |
| 47.11 | 125.60 | 52.29 | 136.57 | 57.47 | 142.39 |
| 47.36 | 126.11 | 52.54 | 137.03 | 57.72 | 142.56 |
| 47.61 | 126.60 | 52.79 | 137.48 | 57.97 | 142.69 |
| 47.85 | 127.10 | 53.03 | 137.88 | 58.21 | 142.84 |
| 48.10 | 127.60 | 53.28 | 138.26 | 58.46 | 142.96 |
| 48.35 | 128.12 | 53.53 | 138.65 | 58.71 | 143.07 |
| 48.59 | 128.64 | 53.77 | 138.99 | 58.95 | 143.19 |
| 48.84 | 129.11 | 54.02 | 139.35 | 59.20 | 143.28 |
| 49.09 | 129.81 | 54.27 | 139.64 | 59.45 | 143.37 |
| 49.33 | 130.39 | 54.51 | 139.95 | 59.69 | 143.44 |
| 49.58 | 130.96 | 54.76 | 140.22 | 59.94 | 143.45 |
| 49.83 | 131.51 | 55.01 | 140.47 | 60.19 | 143.48 |
| 50.07 | 132.09 | 55.25 | 140.70 | 60.43 | 143.49 |
| 50.32 | 132.64 | 55.50 | 140.93 | | |
| | | | | Infinity | 143.49 |

Table 2. *The heat evolved in the form of the extent of reaction (in terms of $\alpha$) vs. time for the first stage of the thermal decomposition at 390.6 K of tetrazene in uncrimped aluminium pans, in a stream of nitrogen.*

| Time (min.) | $\alpha$, % | $\alpha / (100 - \alpha)$ | $\ln [\alpha / (100 - \alpha)]$ |
|---|---|---|---|
| 28.86 | 11.35 | 0.128032 | - 2.05548 |
| 29.35 | 14.09 | 0.164009 | -1.80783 |
| 29.85 | 17.24 | 0.208313 | -1.56871 |
| 30.34 | 20.80 | 0.262626 | -1.33702 |
| 30.83 | 24.72 | 0.328374 | -1.1136 |
| 31.33 | 29.10 | 0.410437 | -0.89053 |
| 31.82 | 33.89 | 0.512630 | -0.66820 |
| 32.31 | 38.98 | 0.638807 | -0.44815 |
| 32.81 | 44.34 | 0.796622 | -0.22737 |
| 33.05 | 47.06 | 0.888931 | -0.11774 |
| 33.55 | 52.58 | 1.108815 | + 0.10329 |
| 33.79 | 55.35 | 1.239642 | 0.21482 |
| 34.04 | 58.08 | 1.385496 | 0.32606 |
| 34.29 | 60.75 | 1.547771 | 0.43682 |
| 34.53 | 63.38 | 1.730748 | 0.54855 |
| 35.03 | 68.30 | 2.154574 | 0.76759 |
| 35.52 | 72.80 | 2.676471 | 0.98450 |
| 36.01 | 76.71 | 3.293688 | 1.19201 |
| 36.36 | 78.49 | 3.649000 | 1.29445 |
| 36.75 | 81.66 | 4.452563 | 1.49248 |
| 37.27 | 84.35 | 5.389776 | 1.68450 |

Linear Least Squares plot of $\ln [\alpha / (100 - \alpha)]$ vs. t (min.), fits the equation
$$\ln [\alpha / (100 - \alpha)] = - 14.8888 + 0.446503\, t \text{ (min.)}$$
with a coefficient of determination of 0.99954

*Table 3.* *The Kinetic Parameters for the Thermal Decomposition of Tetrazene between 387 K and 398 K in a stream of nitrogen and at ambient pressure.*

| Temp., (K) [corr.] | $k_2$ ($min^{-1}$), from Eq. 2 |
| --- | --- |
| 387.9 | 0.2881 |
| 390.0 | 0.3818 |
| 390.4 | 0.4270 |
| 390.6 | 0.4465 |
| 392.9 | 0.5757 |
| 394.9 | 0.8048 |
| 398.0 | 1.2500 |

From these data, a linear plot of $\ln ( k_2 [min^{-1}] )$ vs. $1/T(K)$ is obtained, with an intercept, $\ln ( k_2 [min^{-1}] )$ at $1/T = 0$ K or $\ln A$ ($min^{-1}$), of 56.2336 and a slope of -22.295, with a linear least squares coefficient of determination of 0.9968. This leads to an Arrhenius activation energy for the reaction under investigation of 185.4 kJ $mol^{-1}$, and pre-exponential, $\ln A$ ($min^{-1}$) of 56.2336.

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(between 385 K and 400 K)

Daniel J. Whelan and Mark R. Fitzgerald

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19. ABSTRACT

The efficient explosive pick-up of the AMRL gasless cap composition based on boron / $Pb_3O_4$ / tetrazene and of many in-service stab- and percussion- sensitive compositions based on primary explosive lead salts mixed with tetrazene arises from the explosive behaviour of tetrazene and its functioning as an energetic sensitizer.

Using the thermoanalytical techniques of differential scanning calorimetry and thermogravimetry, it was established that tetrazene decomposes in a series of steps, close to its ignition temperature, ca. 140°C (413 K); initially, it softens, then it decomposes exothermically in a two-stage process, the first and main stage following an autocatalytic rate law of the form

$$d(\alpha)/dt = k_2 \, \alpha \, (1 - \alpha).$$

where $\alpha$ is the degree of reaction in this first stage, and $t$, the time.

From an analysis of the kinetics carried out between 387.9 K and 398 K, it has been shown that the kinetics follow an Arrhenius rate dependency, leading to an activation energy (which can be related to the energetics in the bond-breaking processes) of 185.4 kJ $mol^{-1}$ and a pre-exponential factor, related to the entropy of the reaction, ln A ($min^{-1}$), of 56.23.